It is known that polyglycol ether derivatives, containing on an average 20 to 70, preferably 25 to 40, ethoxylate (—CH₂—CH₂—O—) groups, of primary or secondary amines containing at least one higher aliphatic residue bound to the amino group or water-soluble salts of acid esters which are derived on one hand from polybasic acids and on the other hand from these polyglycol ether derivatives, can be used as levelling agents in wool dyeing. These known levelling agents are conventionally used in an amount of about 0.1 to 8% by weight, advantageously of 0.5 to 3% by weight, calculated on the weight of the material to be dyed.

Good levelling effects are achieved, for example, with polyglycol ether derivatives, containing 25 to 70, more especially about 30, ethoxylate (—CH₂—CH₂—O—) groups, of primary aliphatic monamines of the formula R—NH₂

(1)

in which R represents a higher unsaturated or saturated, branched or preferably linear, saturated aliphatic hydrocarbon radical with at least 16, preferably at most 24, carbon atoms, for example of palmitamide, stearylamine, arachidylamine or behenylamine or of mixtures of such amines, for example of mixtures consisting substantially of amines of the formula

H₂N—(CH₂)ₚ—NH₂

(2)

in which p is an odd number, being at least 15 and at most 21, and at least 20, preferably at least 30, percent by weight of the amines present in the mixture consisting at least 20 carbon atoms, as well as water-soluble salts, more especially sodium and ammonium salts, of acid esters derived on one hand from polybasic acids such as phosphoric, maleic or especially sulphuric acid, and on the other hand from the above-mentioned polyglycol ether derivatives or from polyether derivatives of the formula

\[
\begin{align*}
R_1 & - R_2 \\
N & - CH₂ - CH₂ - CH₂ - N
\end{align*}
\]

(3)

in which \( R_1 \) and \( R_2 \) each represents an aliphatic hydrocarbon radical, where \( R_1 \) contains 12 to 22 and \( R_2 \) at least 11 to 21 carbon atoms, and \( m \) and \( n \) are whole numbers, the sum \( m+n \) being at least 21 and preferably about 31.

While levelling agents of the kind defined above produce very light dyeings on wool fabrics, dyeing of wool yarn with wool dyestuffs, more especially when the wool yarn is dyed in apparatus by the called suspension dyeing method, in the presence of the levelling agents referred to, the wool yarn generally suffers a varying degree of sticking together, as a result of which the dyeing finally obtained is correspondingly patchy.

It has now been found that when wool yarn is dyed with wool dyestuffs using as levelling agents polyglycol ether derivatives, containing on an average 20 to 70, preferably 25 to 40, ethoxylate (—CH₂—CH₂—O—) groups, of primary or secondary amines containing at least one aliphatic radical bond to the amino group, or water-soluble salts of acid esters derived on the one hand from polybasic acids and on the other hand from these polyglycol ether derivatives, more especially when dyeing wool yarn in apparatus by the called suspension dyeing method, the wool yarn in hand form undergoes practically no sticking and very level dyeings can be obtained by using dyebaths which contain in addition to the wool dyestuff and the levelling agent defined above

(a) Paraffin oil in an amount of about 100, preferably about 150, percent by weight, referred to the levelling agent,

(b) An emulsifier for paraffin oil in an amount of at least 5, preferably of about 10 to 25, percent by weight, referred to the paraffin oil, and

(c) A silicone defoaming agent in an amount of at least 0.1% by weight, referred to the levelling agent.

The wool yarn is dyed with wool dyestuffs by the dyeing methods conventionally applied to wool. For this purpose there may be used the usual wool dyestuffs, for example complex chromium or cobalt compounds of monoazo dyestuffs in which 1 atom of chromium or cobalt is bound in complex union to 2 molecules of azo dye-stuff, the molecule of the complex compound consisting of mixtures from any acid groups imparting solubility in water. Preferred use is made of wool dyestuffs that contain at least one acid group imparting solubility in water, that is to say a carboxylic acid group or a sulphonic acid group not participating in the formation of the metal complex, such as acid wool dyestuffs that are free from metal bound in complex union; complex chromium compounds, containing sulphonic acid groups, of monoazo-dyestuffs in which 1 atom of chromium is bound in complex union with 1 molecule of azo dyestuff; water-soluble reactive dyestuffs and complex chromium or cobalt compounds of monoazo dyestuffs in which 1 atom of chromium or cobalt is bound in complex union with 2 molecular of azo dye-stuff, and the molecule of the complex compound may contain one or more than one acid compound imparting solubility in water.

According to the present process wool yarn is dyed in dyebaths that contain in addition to the wool dyestuff and a certain levelling agent the above-mentioned proportions of (a) paraffin oil, (b) an emulsifier for paraffin oil, and (c) a silicone defoaming agent.

Particularly good results are achieved by dyeing wool yarn with wool dyestuffs that contain at least one acid group imparting solubility in water and as levelling agent one of the above-mentioned polyglycol ether derivatives of primary aliphatic monamines of the formulae (1) and (2).

Suitable emulsifiers for paraffin oil—to be used in an amount of at least 5, preferably of about 10 to 25, percent by weight referred to the weight of paraffin oil—are known non-ionic polyglycol ether derivatives, containing 4 to 9 or little more ethoxylate (—CH₂—CH₂—O—) groups, of preferably unsaturated aliphatic compounds that can be hydroxyethylated, more especially of ununsaturated fatty alcohols or fatty acids, for example the adduct of about 6 mols of ethylene oxide with 1 mol of oleyl alcohol, or the adduct of 4 mols of ethylene oxide with 1 mol of oleic acid sorbitan ester, or the esterification product of oleic acid with a polyethylene glycol having a molecular weight of 300; furthermore, non-ionic compounds whose molecule contains fewer than 4 or no ethoxylate groups at all, for example the adduct of 2 to 3 mols of ethylene oxide with 1 mol of oleyl alcohol, or oleyl alcohol itself.

The silicone defoaming agents to be used are organopolysiloxanes, for example alkylphenylpolysiloxanes or more especially alkylpolysiloxanes such as methylpolysiloxanes having at 25°C a viscosity of at least 0.7 centipoise. Preferred silicone defoaming agents are, for example
ample, the methylpolysiloxanes having at 25° C. a viscosity of 50 to 1500, preferably of about 100 to 500, centipoises. Relevant methylpolysiloxanes correspond to the formula

\[
R - \left( \begin{array}{c}
\text{SiO} \\
\text{Si} \\
\text{Si} \\
\text{Si}
\end{array} \right) - R
\]

in which \( R \) represents a methyl or methoxy group, and \( x \) is a whole number greater than 1, being for example 50 to 400 or more. The amount of silicone deforming agent to be used is at least 0.1% by weight, for example 0.7 to about 10% by weight, referred to the weight of the levelling agent. While an addition of more than 10% of deforming agent is not harmful, it does not offer any advantage over the specified smaller amounts either.

The above-defined levelling agent, the paraffin oil, the emulsifier for paraffin oil and the silicone deforming agent may be added separately to the dyebath. However, it is preferable to use a stable, more especially an aqueous, preparation containing the correct proportions of levelling agent, paraffin oil, emulsifier, silicone deforming agent and, if desired, further assistants, and this preparation is added to the dyebath.

Accordingly, the present invention includes also stable, more especially aqueous, preparations suitable for dyeing wool yarn with wool dyestuffs by the present process, said preparations containing in addition to the levelling agent of the kind defined above

(a) Paraffin oil in an amount of over 100, preferably of about 150, percent by weight, referred to the levelling agent,

(b) An emulsifier for paraffin oil in an amount of at least 5, preferably of about 10 to 25, percent by weight, referred to the paraffin oil, and

(c) A silicone deforming agent in an amount of at least 0.1% by weight, referred to the levelling agent.

When wool yarn is dyed by the present process very level shades are obtained. The present process is of special value in cases where the previously known methods cause sticking of the wool yarn and as a result the dyes may easily turn out patchy.

Parts and percentages in the following examples are by weight.

Example 1

100 kg of wool yarn are pre-wetted at 15° C. for 5 minutes in 2000 litres of water in a bank dyeing apparatus (single pole suspension system), whereupon 2 kg of glacial acetic acid, 10 kg of crystalline sodium sulfate, 4 kg of Preparation A as described below and 1 kg of the dyestuff of the formula

\[
\text{H}_2\text{C} = \text{C}-\text{OH} \quad \text{O} \quad \text{C}-\text{H}_3\text{O} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{H}_3\text{C} \quad \text{O} \\
\text{O}_2\text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{H}_3\text{C} \quad \text{O} \quad \text{N}_2\text{O} \quad \text{O}_2\text{N} \quad \text{N} \quad \text{N} \quad \text{H}_3\text{C} \quad \text{O}
\]

are added. The temperature is raised to the boil within 45 minutes and the yarn is dyed for one hour at the boil, then cooled, rinsed in cold water and dried.

The yarn is dyed a level blue shade and does not tend to stick.

Preparation A can be manufactured thus:

20 parts of the reaction product of 30 mols of ethylene oxide with 1 mol of a mixture of primary alkylamines containing about 10% of stearylamine, 55% of arachidylamine and 35% of behenylamine, are melted at 60° C. and neutralised with 0.6 part of glacial acetic acid; 6 parts of the adduct of 6 mols of ethylene oxide with 1 mol of oleyl alcohol (emulsifier) and 30 parts of paraffin oil are then added. While stirring the mixture at about 60° C., 24.4 parts of water are run in portionwise; the whole is cooled to 30 to 40° C. and mixed with 0.08 part of methylpolysiloxane (silicone deforming agent) in the form of an aqueous emulsion. A thick, white paste is obtained.

Instead of the acid anthraquinone dyestuff used in the above example, where may be used the acid dyestuff of the formula

\[
\text{H}_2\text{C} - \text{C} = \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \\
\text{HO}_2\text{C} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH}
\]

which produces scarlet shades.

Example 2

100 kg of wool yarn are pre-wetted for 10 minutes at 50° C. in 1000 litres of water in a bank dyeing apparatus, whereupon 2 kg of glacial acetic acid, 10 kg of crystalline sodium sulfate, 4 kg of Preparation B as described below and 1 kg of the 1:2-chromium complex compound of the monoazo dyestuffs of the formula

\[
\text{H}_2\text{C} = \text{C}-\text{OH} \quad \text{O} \quad \text{C}-\text{H}_3\text{O} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{H}_3\text{C} \quad \text{O} \\
\text{O}_2\text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{H}_3\text{C} \quad \text{O} \quad \text{N}_2\text{O} \quad \text{O}_2\text{N} \quad \text{N} \quad \text{N} \quad \text{H}_3\text{C} \quad \text{O}
\]

which dyes wool yarn red-brown shades, are added.

The temperature is raised to the boil within 45 minutes and the yarn is dyed for one hour at the boil, then cooled, rinsed in cold water and dried. A level red-brown dyeing is obtained, and the wool yarn does not tend to stick.

Preparation B can be manufactured thus:

A mixture of 92 parts (1 mol) of a commercial propylenediamine in which one amino group contains the hydrocarbon residue corresponding to soybean fatty acid, 70.5 parts (1 mol) of oleic acid and 0.5 part of para-toluensulfonic acid is boiled with stirring in a reactor equipped with a descending condenser for 6 to 8 hours at 160 to 170° C. under a pressure of 100 mm. Hg, with water passing over, to yield 155 parts of the acylation product (1).

139 parts (1 mol) of the resulting acylation product (1) are reacted with 212 parts (22 mols) of ethylene oxide in the presence of 1.4 parts of sodium under nitrogen at 160 to 170° C.

32 parts of this ethylene oxide adduct are mixed in a reactor provided with an agitator within 15 minutes at 60° C. with 4.4 parts of urea and then within 30 minutes with 4.4 parts of amidosulfonic acid. The bath is kept for 6 hours on a boiling water bath, whereupon 38 parts of paraffin oil and 3.8 parts of the adduct of 6 mols of ethylene oxide with 1 mol of oleyl alcohol (emulsifier) are added. In the course of about 30 minutes at 60° C., 24 parts of water are stirred in portionwise, the whole is cooled to 30° C. and mixed with 0.08 part of silicone deforming agent (methylpolysiloxane) in the form of an aqueous emulsion. The resulting Preparation B contains about 30% of the ammonium salt of the acid sulfonic acid ester of the above-mentioned ethylene oxide adduct (levelling agent).

Instead of the red-brown-dyeing 1:2-chromium complex compound used in the above example there may be
used the 1:2-cobalt complex of the dyestuff of the formula

(9)

Similar, good results are obtained when in this example Preparation B is replaced by an equal amount of the Preparation C or D described below.

Preparation C: 80 parts of the reaction product of 30 mols of ethylene oxide with 1 mol of a commercial mixture of primary akylaminos containing about 10% of stearylamine, 55% of arachidylamine and 35% of behenylamine, are melted at 60° C. and neutralised with 2.4 parts of glacial acetic acid. The melt is mixed with 120 parts of paraffin oil, 14.5 parts of oleyl alcohol and 14.5 parts of the adduct of 6 mols of ethylene oxide with 1 mol of oleyl alcohol (emulsifier). While stirring the mixture at 60° C., 116 parts of water are added portionwise with

in 30 minutes and the whole is mixed with 2 to 5 parts of methylpolysiloxyane (silicone defoaming agent). A fine emulsion is obtained.

Preparation D: 80 parts of the reaction product of 30 mols of ethylene oxide with 1 mol of a commercial mixture of primary akylamines containing about 30% of palmitylamine, 40% of stearylamine, 20% of arachidylamine and 10% of behenylamine are melted at 60° C. and neutralised with 2.4 parts of glacial acetic acid. The melt is then mixed with 120 parts of paraffin oil, 14.5 parts of oleyl alcohol and 14.5 parts of the adduct of 6 mols of ethylene oxide with 1 mol of oleyl alcohol (emulsifier). While stirring the whole at 60° C., there are added within 30 minutes 116 parts of water in portions, and the batch is then mixed with 2 to 5 parts of methylpolysiloxane (silicone defoaming agent). A fine emulsion is obtained.

Example 3

100 kg. of wool yarn are pre-wetted for 5 minutes at 30° C. in 2000 litres of water in a hank dyeing apparatus, whereupon there are added 2 kg. of glacial acetic acid, 10 kg. of crystalline sodium sulfate, 4 kg. of Preparation E described below and 500 g. of the red-dyeing acid dye-stuff of the formula

Within 30 minutes the temperature is raised to the boil and the yarn is dyed for one hour at the boil, then cooled, rinsed in cold water and dried.

A very level red shade is obtained. The wool yarn shows no sticking tendency.

Preparation E can be manufactured thus:

Within 20 minutes the whole is heated to 85° C., maintained for 20 minutes at this temperature, raised within 15 minutes to the boil and kept for 1 hour at the boil. The bath is then mixed with 3 kg. of 25% aqueous ammonium hydroxide solution; the yarn is treated for 15 minutes in the cooling liquor, rinsed in cold water and dried.

A strong, level blue shade is obtained. The wool yarn has no tendency to stick.

Instead of the blue-dyeing dyestuff used in the above example there may be used the blue-dyeing copper phthalocyanine trisulfonic acid.

Similar, good results are obtained when Preparation C is replaced by an identical amount of Preparation E described in Example 3.

What is claimed is:

1. Process for dyeing wool yarn with wool dyestuffs in the presence of a levelling agent (A), which process comprises dyeing the wool yarn in an aqueous dyebath containing in addition to the wool dyestuff and levelling agent (A)

   (I) paraffin oil in an amount of at least 100 percent by weight, referred to the weight of the levelling agent (A),

   (II) an emulsifying agent for paraffin oil in an amount of at least 5 and at most 25 percent by weight, referred to the weight of the paraffin oil, and

   (III) a defoamer of the silicone-type in an amount of at least 0.1 percent by weight, referred to the weight of the levelling agent (A),

   the levelling agent (A) being a polyglycol ether derivative of an at most secondary higher fatty monoamine, said polyglycol ether derivative containing 25 to 40 etheroxy groups, and the wool dyestuff being one which contains at least one acid group imparting solubility in water.

2. Process for dyeing wool yarn with wool dyestuffs in the presence of a levelling agent (A), which process comprises dyeing the wool yarn in an aqueous dyebath containing in addition to the wool dyestuff and levelling agent (A)
(I) paraffin oil in an amount of 100 to 150 percent by weight, referred to the weight of the levelling agent (A),
(II) an emulsifying agent for paraffin oil in an amount of at least 5 and at most 25 percent by weight, referred to the weight of the paraffin oil, and
(III) a defoamer of the silicone-type in an amount of 0.1 to 10 percent by weight, referred to the weight of the levelling agent (A).

the levelling agent (A) being a polyglycol ether derivative of an at most secondary higher fatty monoamine, said polyglycol ether derivative containing 25 to 40 \(-\text{CH}_2\text{-CH}_2\text{-O-}\) (ethoxy) group, and the wool dye-stuff being one which contains at least one acid group imparting solubility in water.

3. Process for dyeing wool yarn with wool dyestuffs in the presence of a levelling agent (A), which process comprises dyeing the wool yarn in an aqueous dyebath containing in addition to the wool dyestuff and levelling agent (A)

(I) paraffin oil in an amount of 100 to 150 percent by weight, referred to the weight of the levelling agent (A),
(II) an emulsifying agent for paraffin oil in an amount of at least 5 and at most 25 percent by weight, referred to the weight of the paraffin oil, and
(III) a defoamer of the silicone-type in an amount of 0.1 to 10 percent by weight, referred to the weight of the levelling agent (A).

the levelling agent (A) being a polyglycol ether derivative of a mixture of amines consisting substantially of amines of the formula

\[
\text{H}_2\text{C-(CH}_2\text{n-NH}_2
\]

wherein \(n\) represents a whole positive number of at least 15 and at most 21, and at least 20 percent by weight of the amines present in the mixture having at least 20 carbon atoms, said polyglycol ether derivative containing about 30 \(-\text{CH}_2\text{-CH}_2\text{-O-}\) (ethoxy)-groups, and the wool dye-stuff being one which contains at least one acid group imparting solubility in water.

4. A stable aqueous dyeing assistant preparation suitable for use in dyeing wool yarn with wool dyestuffs in the presence of a levelling agent, said preparation containing a levelling agent (A) and

(I) paraffin oil in an amount of at least 100 percent by weight, referred to the weight of the levelling agent (A),
(II) an emulsifying agent for paraffin oil in an amount of at least 5 and at most 25 percent by weight, referred to the weight of paraffin oil, and
(III) a defoamer of the silicone-type in an amount of at least 0.1 percent by weight, referred to the weight of the levelling agent (A).

the levelling agent (A) being a polyglycol ether derivative of an at most secondary higher fatty monoamine, said polyglycol ether derivative containing 25 to 40 \(-\text{CH}_2\text{-CH}_2\text{-O-}\) (ethoxy) group, and the wool dye-stuff being one which contains at least one acid group imparting solubility in water.

5. A stable aqueous dyeing assistant preparation suitable for use in dyeing wool yarn with wool dyestuffs in the presence of a levelling agent, said preparation containing a levelling agent (A) and

(I) paraffin oil in an amount of 100 to 150 percent by weight, referred to the weight of the levelling agent (A),
(II) an emulsifying agent for paraffin oil in an amount of at least 5 and at most 25 percent by weight, referred to the weight of the paraffin oil, and
(III) a defoamer of the silicone-type in an amount of 0.1 to 10 percent by weight, referred to the weight of the levelling agent (A),

the levelling agent (A) being a polyglycol ether derivative of an at most secondary higher fatty monoamine, said polyglycol ether derivative containing 25 to 40 \(-\text{CH}_2\text{-CH}_2\text{-O-}\) (ethoxy) groups.

6. A stable aqueous dyeing assistant preparation suitable for use in dyeing wool yarn with wool dyestuffs in the presence of a levelling agent, said preparation containing a levelling agent (A) and

(I) paraffin oil in an amount of 100 to 150 percent by weight, referred to the weight of the levelling agent (A),
(II) an emulsifying agent for paraffin oil in an amount of at least 5 and at most 25 percent by weight, referred to the weight of the paraffin oil, and
(III) a defoamer of the silicone-type in an amount of 0.1 to 10 percent by weight, referred to the weight of the levelling agent (A),

the levelling agent (A) being a polyglycol ether derivative of a mixture of amines consisting substantially of amines of the formula

\[
\text{H}_2\text{C-(CH}_2\text{n-NH}_2
\]

wherein \(n\) represents a whole positive number of at least 15 and at most 21, and at least 20 percent by weight of the amines present in the mixture having at least 20 carbon atoms, said polyglycol ether derivative containing about 30 \(-\text{CH}_2\text{-CH}_2\text{-O-}\) (ethoxy)-groups.

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